1,138,287

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

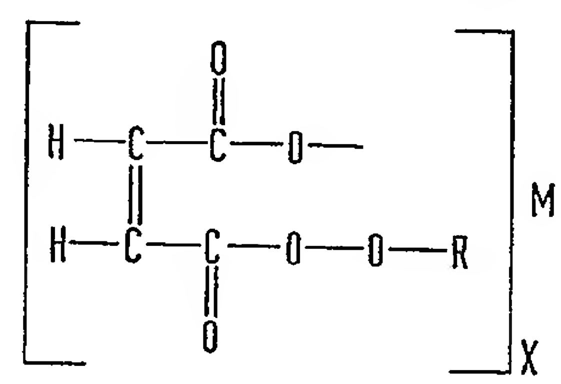
Process for Polymerizing Methyl Methacrylate-Containing Syrups

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polymerization and curing of methyl methacrylate-containing syrups. More particularly, it relates to the improved, more rapid production of articles of polymeric methyl methacrylate, e.g., methacrylate homopolymer and copolymers of methyl methacrylate with α,β-ethylenically unsaturated compounds.

In the production of articles of polymeric methyl methacrylate and, more specifically, in the curing of polymerization of the monomers involved for producing the polymeric articles, the most important step is the curing of the methyl methacrylate-containing syrup. For this step it is necessary to use a catalyst, or, as it is sometimes called, an initiator. As catalysts, the prior art has suggested the use of peroxy compounds such as diethyl peroxide and benzoyl peroxide, as disclosed in British Patent 870,191 and U.S. Patent 3,154,600. Recently, the use of the hemi-perester of maleic acid has been disclosed in German Patent 1,068,467 as a useful catalyst for the polymerization and curing of methyl methacrylate-containing syrups. However, we have found that this catalyst, though quite effective, operates rather slowly. Thus, curing times of over four hours are not uncommon in the preparation of articles of the methyl methacrylate homopolymer when curing at or near room temperature. The invention has as its object to provide methods for curing methyl methacrylate-containing syrups which overcome the deficiencies of the known prior art methods.

According to the invention a syrup containing 10—35% by weight of methyl methacrylate polymer having an inherent viscosity of 0.25—1.0 dissolved in monomeric methyl methacrylate is cured in the presence of from 0.05—5 mole per cent (preferably 0.1—1 mole per cent) based on the number of moles of monomeric methyl methacrylate in the syrup, of a metal salt of a hemi-perester of maleic acid having the formula



wherein

- M is a metal, preferably selected from the group consisting of Group I A metals* (sodium, potassium, lithium, etc.), Group II A metals* (calcium, magnesium, strontium, barium, etc.), zinc, lead, cobalt, nickel, manganese, and copper;
- x is an integer that has a value of 1 or more up to and including the valence of the metal; and
- R is a saturated tertiary alkyl radical, preferably tertiary butyl.

Where "x" is an integer that is less than the valence of metal, the other valence or valences of the metal may be satisfied by hydroxyl or the anion of the metal compound originally used or other anion available in the system.

**Handbook of Chemistry and Physics*, 42nd Edition, Chemical Rubber Publishing Co., Ohio (1960—1961), pp. 448—449.

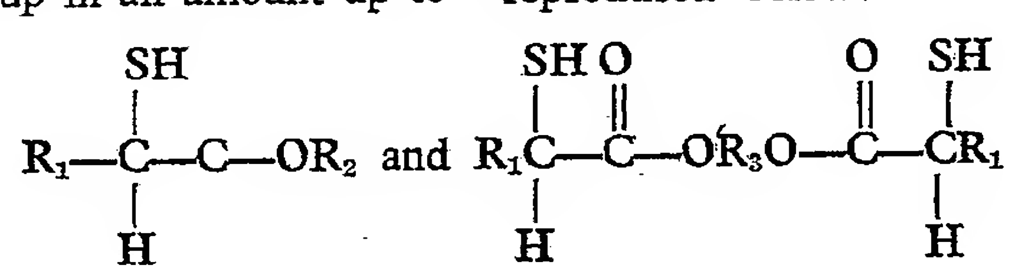
[*Price 4s. 6d.*]

The starting syrup or polymer-in-monomer solution may be prepared by any of the methods described in British Patent No. 870,191 or U.S. Patent No. 3,154,600. Specifically, the syrup may be made by heating a small amount of a polymerization initiator in solution in the methacrylic ester and in the presence of a chain transfer agent at a suitable pressure and temperature. Heating is continued until the solution reaches a predetermined viscosity. Thereafter, the hot solution is quenched by the addition of cold monomer containing a polymerization inhibitor. More specifically, a syrup having a viscosity of 0.5—50 poises at 25°C. can be produced from methyl methacrylate by heating the monomeric methyl methacrylate in a jacketed kettle at a temperature of 50—150°C. under refluxing conditions. Atmospheric pressure is used and the refluxing material is stirred. Heating is conducted in the presence of a very small amount of initiator and from 0.05—1.0 mole per cent of a chain transfer agent such as the alkyl mercaptans and the mercaptans described in U.S. Patent No. 3,154,600. When a bulk viscosity in the range of 0.5 to 50 poises, which corresponds to an inherent viscosity of 0.25—1.0, is attained and the initiator content has been reduced substantially to zero, i.e., below 20 parts per million, the polymerization is stopped by cooling in any suitable manner. One method of cooling involves adding 1—10% by weight of cold methyl methacrylate containing sufficient hydroquinone or other polymerization inhibitor to inhibit further polymerization of the methyl methacrylate. For the purpose of the present invention, the final solution contains 10—35% by weight of the methyl methacrylate polymer dissolved in the methyl methacrylate monomer. The polymer has an inherent viscosity of 0.25—1.0. By "inherent viscosity" as used herein we mean the inherent viscosity determined at 20°C using a solution of 0.50 grams of the polymer per 100 milliliters of chloroform in accordance with the method described in F. W. Billmeyer, Textbook of Polymer Chemistry, Interscience Publishing Inc. (1957), p. 128. The polymer may also be a copolymer involving a major portion of the methyl methacrylate monomer with such monomers as vinyl acetate, styrene, methyl acrylate, ethyl acrylate, butyl acrylate, cyclohexyl acrylate, ethyl methacrylate, butyl methacrylate and cyclohexyl methacrylate.

The syrup may also contain a cross-linking agent, added to the syrup in an amount up to 20% by weight upon completion of quenching. Any suitable poly-unsaturated, cross-linking agent may be used, e.g., ethylene dimethacrylate, propylene dimethacrylate, polyethylene glycol dimethacrylate, divinyl benzene, triallyl cyanurate, and diallyl phthalate. If desired, a portion, i.e., up to about 2% of the cross-linking agent may be added to the syrup prior to quenching.

Specifically, the process of this invention involves adding to the polymer-in-monomer solution the hemi-perester of maleic acid, e.g., monotertiary butyl peroxymaleate sometimes referred to as t-butyl permaleic acid in combination with a basic compound of the desired metal. As such basic compounds, one may use any metal compound that will react with the acid substituent of the hemi-perester to form the metal salt of the hemi-perester. Such basic compounds include but are not limited to the oxides or hydroxides of the metals; the carbonates of sodium, potassium or zinc; the acetates of sodium, potassium, copper, strontium, magnesium, lead, cobalt, manganese; the acid phthalates, bicarbonates, benzoates, phosphates, sulfides and methacrylates, of sodium and potassium. Although it is most practical to add the basic compound after first dissolving the hemi-perester of maleic acid in the polymer-in-monomer syrup, it is not essential. In fact, a very useful mode of conducting the process involves the dissolution of the hemi-perester in one portion of the syrup and the suspension of the basic compound in another portion of the syrup. As long as the two portions are kept separate, they each will have relatively long pot lives. However, when they are mixed or fed as two streams into a common container, rapid curing results. The curing is accomplished in any case autogenically by merely exposing the syrup containing the metal salt of the hemi-perester of maleic acid to air at a temperature of 15—40°C. Although elevated temperatures and higher pressures may be used, they are not necessary.

In a particularly impressive process from the stand-point of rapidity of the curing, a small residual amount of the mercaptan chain transfer agent used in preparing the syrup is retained for the curing step. Thus, the curing or polymerization of the syrup is carried out in the presence of the mercaptan and the metal salt of the hemi-perester of maleic acid. The most useful mercaptans are those disclosed in U.S. Patent 3,154,600. Their structure is reproduced below:



in which the R groups consist of the following substituents:

R_1 = hydrogen, alkyl, aryl, carboxymethyl, carboalkoxymethyl,

R_2 = hydrogen, alkyl, aryl, alkoxyalkyl, alkoxyalkoxyalkyl, and

R_3 = alkylene, polyalkylene, alkylene oxide and polyalkylene oxide.

Some specific chain transfer agents include glycol dimercaptoacetate and isooctyl mercaptoacetate.

The syrup may be mixed with as much as 85% by weight of an inert solid additive without adversely affecting the improvements obtained by the process of this invention. Such additives include glass fibers, powdered metals, inert particles, pigments, natural and synthetic fibers and any other toughening, filling, coloring or strengthening materials. Such fillers can be any of those that do not interfere with the polymerization of the acrylic resin.

The syrups of the present invention including the metal salt of the hemi-perester of maleic acid may be used to fabricate all types of polymeric articles. Thus, the syrup may be poured on a corrugated surface to produce sheets. The syrups may be poured into molds or over fabrics, metals or layers of glass to provide useful products. The syrup may also be used as a laminating layer for wood and other plastics.

The preferred hemi-perester for forming the metal salt thereof, as stated previously, is monotertiary butyl peroxymaleate. However, other useful hemi-peresters include those where the saturated tertiary alkyl of the hemi-perester is t-amyl, 1-methylcyclohexyl and p-menthyl. The metal salt of the hemi-perester of the difunctional acid should usually be present in an amount greater than 0.05 mole per cent, based on the number of moles of monomeric methyl methacrylate in the syrup, in order to obtain the advantages of the present invention. No additional advantage seems to be obtained by adding more than 5 mole per cent percentage of the salt. If desired, other initiators may be used with the critical metal salt of the hemi-perester. In addition, curing aids may be used. These include the chlorides of antimony and soluble copper salts as disclosed in British Specification No. 922,448 and the chlorides of tin.

The important improvements obtained by the present invention will be more clearly understood by referring to the examples which follow. These examples which illustrate specific embodiments of the present invention should not be construed to limit the invention in any way. Parts and percentages are by weight.

Examples 1—11

A syrup of 30% methyl methacrylate homopolymer in methyl methacrylate monomer, the polymer having an inherent viscosity of about 0.37 is prepared by partial polymerization in situ using glycol dimercaptoacetate as chain transfer agent substantially in the manner described in Example II of U.S. Patent 3,154,600. To 100 parts of this syrup which contains a small residual amount of the mercaptan is added 0.5 part of monotertiary butyl peroxymaleate. In all examples except the Control, one part of a finely divided basic compound is also added and mixed with the syrup to produce the metal salt of the hemi-perester. A portion of each mixture is placed in a "Gel Time" apparatus manufactured by Sunshine Scientific Company, Philadelphia, Pennsylvania and the gel times are determined at 40°C. The results are presented in Table I.

Example 12

To 100 parts of the syrup of Example 1 is added 0.75 part of t-butyl peroxymaleic acid, 150 parts of a precipitated calcium carbonate having an average particle size of 7 microns, and various amounts of finely divided calcium hydroxide, the latter forming various amounts of the calcium salt of the hemi-perester of the maleic acid. The mixture is stirred, poured onto a tray and allowed to stand open to the air at room temperature. The speed of curing is determined by inserting a thermocouple in the mixture and measuring the interval between mixing and the time at which the mixture arrives at its peak temperature. The results are presented in Table II.

TABLE I

Example	Metal salt of hemi-perester	Basic compound	Average Gel time (minutes)
1	calcium	hydroxide	3.9
	,,	oxide	21.7
2	sodium	acetate	11.1
	,,	aluminate	20.3
	,,	benzoate	13.3
	,,	carbonate	10.2
	,,	bicarbonate	53.3
	,,	cyanide	7.9
	,,	thiocyanate	33.9
	,,	formate	21.4
	,,	methacrylate	14.2
	,,	methoxide	6.4
	,,	dihydrogen phosphate	22.7
	,,	orthophosphate	9.8
	,,	stearate	12.1
	,,	sulfide	13.9
3	potassium	carbonate	12.4
4	magnesium	acetate	14.9
	,,	hydroxide	27.8
	,,	oxide	32.1
5	barium	hydroxide	13.7
6	copper	acetate	61.4
7	strontium	acetate	43.5
	,,	hydroxide	7.7
8	zinc	acetate	6.8
9	lead	acetate	4.5
10	cobalt	acetate	50.6
11	manganese	acetate	8.7
Control	(hydrogen)	NONE	greater than 275

TABLE II

Hemi-perester (parts)	Calcium Hydroxide (parts)	Exotherm Time (minutes)
0.75	7.50	14
0.75	3.00	13
0.75	1.50	12
0.75	0.75	13
0.75	0.30	11
0.75	0.15	18
0.75	None	168

EXAMPLE 13

The procedure of Example 12 is repeated using only 0.15 parts of the hemi-perester of maleic acid and various amounts of calcium hydroxide. The "exotherm times" are measured as in Example 12 and the results are presented in Table III.

TABLE III

Hemi-perester (parts)	Calcium Hydroxide (parts)	Exotherm Time (minutes)
0.15	0.45	39
0.15	0.30	48
0.15	0.15	50
0.15	0.075	56

EXAMPLE 14

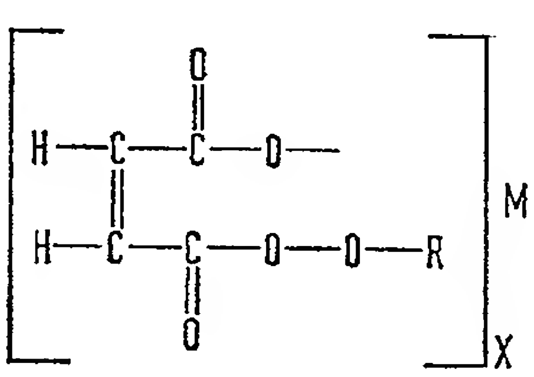
The procedure of Example 12 is again repeated after first making certain that the syrup contained no residual mercaptan. In the following table, Table IV, the results obtained without any residual mercaptan are compared to the results obtained in Example 12 where residual mercaptan is present.

TABLE IV

Example	Hemi-perester (parts)	Calcium Hydroxide (parts)	Exotherm Time (minutes)
14	0.75	1.5	79
12	0.75	1.5	12
Control	0.75	None	168

WHAT WE CLAIM IS:—

1. Process for production of articles of polymeric methyl methacrylate which comprises curing a syrup containing 10—35% by weight of methyl methacrylate polymer dissolved in monomeric methyl methacrylate, the polymer having an inherent viscosity (as herein defined) of 0.25—1.0, in the presence of from 0.05 to 5 mole per cent, based on the number of moles of monomeric methyl methacrylate in the syrup, of a metal salt of a hemi-perester of maleic acid having the formula



wherein

M is a metal;

x is an integer having a value of from 1 to the valence of the metal; and

R is a saturated tertiary alkyl radical.

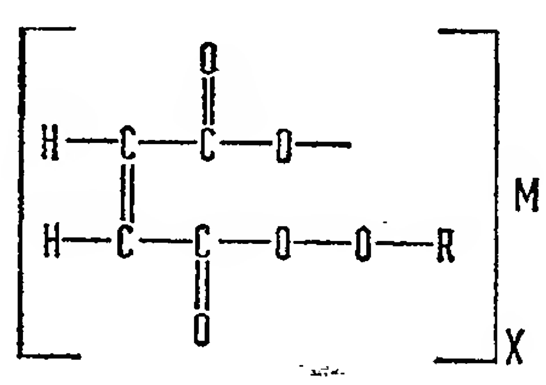
2. Process according to Claim 1 wherein the methyl methacrylate polymer is methyl methacrylate homopolymer.

3. Process according to Claim 1 or 2 wherein the metal is sodium, potassium, lithium, calcium, magnesium, strontium, barium, zinc, lead, cobalt, nickel, manganese or copper.

4. Process according to Claim 3 wherein the metal is calcium.

5. Process according to Claims 1 to 3 wherein the tertiary alkyl radical is tertiary butyl.

6. A mixture for preparing polymeric methyl methacrylate articles consisting essentially of a syrup containing 10—35% by weight of methyl methacrylate polymer dissolved in monomeric methyl methacrylate, the polymer having an inherent viscosity (as herein defined) of 0.25—1.0, and from 0.05 to 5 mole percent, based on the number of moles of monomeric methyl methacrylate in the syrup, of a metal salt of a hemi-perester of maleic acid having the formula



wherein

M is a metal;

x is an integer having a value of from 1 to

the valence of the metal; and

R is a saturated tertiary alkyl radical.

7. A mixture according to Claim 6 wherein the methyl methacrylate polymer is methyl methacrylate homopolymer.

8. A mixture according to Claim 6 or 7 wherein the metal is sodium, potassium, lithium, calcium, magnesium, strontium, barium, zinc, lead, cobalt, nickel, manganese or copper.

9. A mixture according to Claim 8 wherein the metal is calcium.

10. A mixture according to any of Claims 6 to 9 wherein the tertiary alkyl radical is tertiary butyl.

11. A mixture according to any of Claims 6 to 9 wherein the syrup has been prepared by polymerising methyl methacrylate in the presence of from 0.05 to 1.0 mole percent of a mercaptan chain transfer agent.

12. Process according to claim 1 wherein there is used as syrup a mixture claimed in any of claims 6 to 11.

13. Process for production of articles of polymeric methyl methacrylate according to Claim 1, substantially as disclosed in any of Examples 1 to 14.

14. Articles of polymeric methyl methacrylate whenever produced in accordance with the process set forth in any of Claims 1 to 5, 12 or 13.

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